

CO Sensors for Reformate Powered Fuel Cells

R. Mukundan, Eric Brosha, and D.R. Brown Research Staff
Fernando Garzon Team Leader
MST-11 Group
Los Alamos National Laboratory
Los Alamos NM 87545 USA



Objectives

- Reformate gas powered fuel cell systems require sensors for carbon monoxide level monitoring and feedback control
 - A high temperature sensor is required for measurement of 0.1 to 2% CO in reformate gas for fuel processor control
 - A low temperature sensor for measuring 10-100 ppm range concentrations for stack poisoning control



Approach

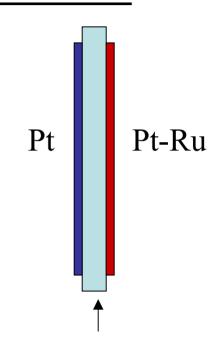
- Two different electrochemical sensor types are being investigated for high and low temperature CO sensing
 - An oxide solid electrolyte device is being developed for the high temperature application
 - Yttria stabilized zirconia oxygen ion conducting electrolyte
 - Strontium yttrium zirconium perovskite proton conducting electrolyte
 - Low temperature amperometric device based on CO inhibition of hydrogen oxidation kinetics
 - Perfluorosulfonic acid polymer electrolyte
 - Inorganic acid electrolyte



Approach

Low temperature Amperometric Sensor

- Use Nafion as the proton conducting membrane
- Use Pt or Ru electrode as working electrode
 - is sensitive to CO poisoning
- Use Pt-Ru electrode as a counter electrode
 - more tolerant to the presence of CO



Proton conducting membrane



Project Timeline

Fy01 Fy02 Fy03 Fy04

Project begins

Low temp CO sensor prototype developed Sense 100-1000ppm CO in H2

> High temp CO sensors first prototypes made Sense 1-500ppm CO in Room Air

Oxide proton conductor thin film technology developed

Ellucidated the working principle of these low temperature sensors

Improved Low Temperature sensor Works at Room Temperature Stable response to 10-200ppm CO in H2

Oxide based amperometric sensors do not have sensitivity to CO and Oxide based mixed-potential sensors do not operate stabily in the presence of H2

Continue work on the low Project ends temperature sensors to optimize sensor response, stability and response time

Materials Science and Technology, Electronics Research (MST-11)

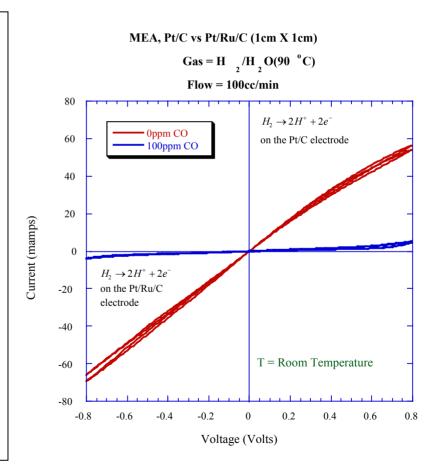


- Effect of CO on typical fuel cell electrode loadings
 - Working Electrode
 - Pt/C/Nafion: 0.22mg/cm² of Pt or
 - Ru/C/Nafion : 0.12mg/cm² of Ru
 - Reference Electrode
 - Pt/Ru/C/Nafion: 0.25mg/cm² of Pt/Ru(50/50)alloy
 - Electrolyte
 - Nafion 1135



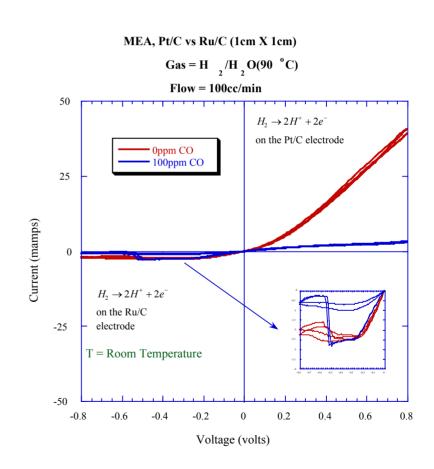
 Both the Pt/C and the Pt/Ru/C electrodes are good at hydrogen oxidation and both of them get poisoned by the CO

- The CO poisoning is not easily reversible
 - Recovery takes hours without air bleeding





- While the Pt/C electrode is good at hydrogen oxidation the Ru/C electrode is not very efficient at H₂ oxidation
- Both the electrodes get poisoned by the CO, the Ru/C electrode to a lesser extent
- The CO from the Ru/C electrode can be easily stripped at voltages <-0.5V (see inset)
- The CO poisoning is not easily reversible on the Pt/C electrode
 - Recovery takes hours without air bleeding

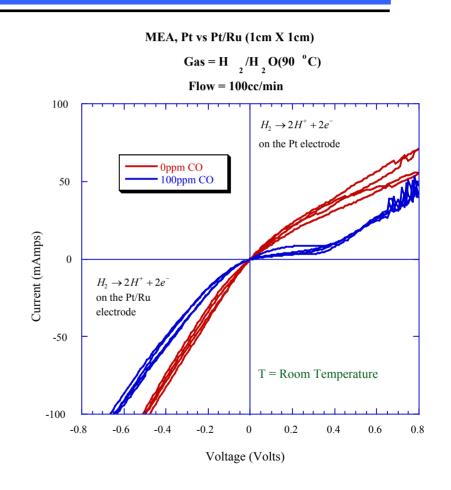




- Effect of CO on sensor response at high catalyst loadings
 - Working Electrode
 - Pt/Nafion : $\approx 10 \text{mg/cm}^2$ of Pt or
 - Ru/Nafion : $\approx 10 \text{mg/cm}^2$ of Ru
 - Reference Electrode
 - Pt/Ru/Nafion : $\approx 10 \text{mg/cm}^2$ of Pt/Ru(50/50)alloy
 - Electrolyte
 - Nafion 117

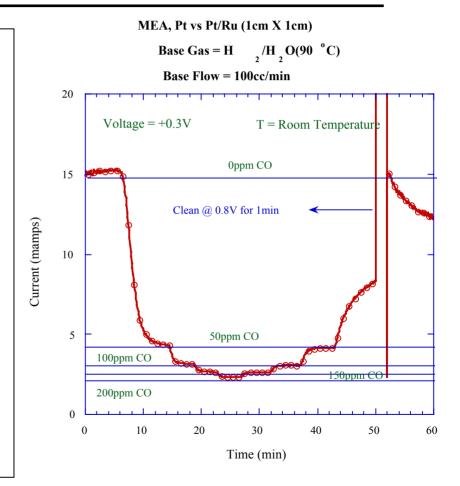


- Both the Pt and Pt/Ru alloy electrodes are good for H₂ oxidation
- There is very little effect of CO on the Pt/Ru alloy electrode.
 - This electrode could serve as a pseudo-reference electrode
- The Pt electrode gets poisoned by the CO which can easily be cleaned at voltages > 0.4V





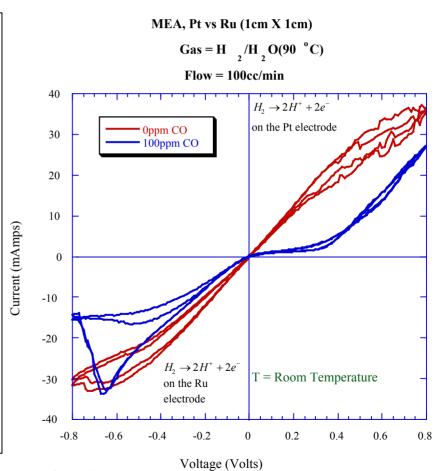
- The extent of poisoning on the Pt electrode can be used to give a useful sensor response
- The current at 0.3V decreases from 15mamps to <5mamps when the CO content in the H₂ stream is increased from 0 to 50ppm.
- The final CO can be cleaned by applying a 0.8V potential for approx. one minute



Materials Science and Technology, Electronics Research (MST-11)

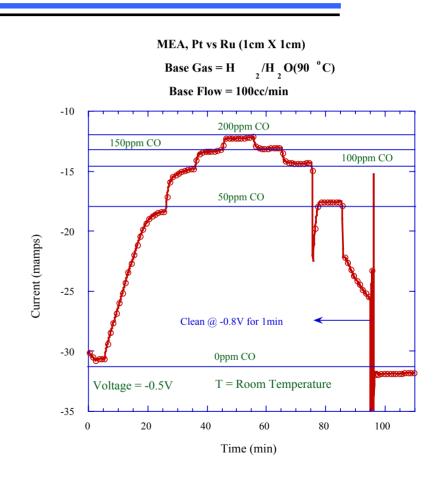


- Both the Pt and Ru electrodes are good for H₂ oxidation
- The Pt electrode gets poisoned by the CO which can easily be cleaned at voltages > 0.4V
- The Ru electrode also gets poisoned by the CO and can be cleaned at voltages < -0.6V
 - The clean up on this electrode appears to be slower than that of the Pt/Ru alloy electrode





- The extent of poisoning on the Ru electrode can be used to give a useful sensor response
- The current at -0.5V decreases from -30mamps to -18mamps when the CO content in the H₂ stream is increased from 0 to 50ppm.
- The final CO can be cleaned by applying a -0.8V potential for approx. one minute





Future Plans

- Study the stability of these sensors at room temperature
- Increase the operating temperature of these sensors to 80-90°C
- Study water management issues in these sensors and stabilize the sensor response at elevated temperatures
- Optimize electrodes and electrolyte to get maximum sensitivity to CO



Acknowledgements

- DOE-OAAT for Funding
- Francisco Uribe for help with CV's
- Bryan Pivovar and Piotr Zelenay for insights and assistance with the Pt-Ru membranes
- Judith Valerio for assistance with the carbon-supported electrodes